CLARK

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FICHTELIT.
A FOSSIL
CARBO-HYDROGEN

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1857

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FICHTELIT.

A FOSSIL CARBO-HYDROGEN

FOUND IN THE

FICHTELGEBIRGE OF NORTH-BAVARIA.

INAUGURAL DISSERTATION
PREPARED FOR PROMOTION TO THE DEGREE OF
DOCTOR OF PHILOSOPHY,
AND ADDRESSED
TO THE PHILOSOPHICAL FACULTY
OF THE
GEORGIA AUGUSTA UNIVERSITY AT GOETTINGEN,
BY

T. EDWARDS CLARK B. S.
OF CAMBRIDGE MASSACHUSETTS, U. S. A.

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1857
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TO

PROFESSOR VON LIEBIG,

THIS

DISSERTATION IS DEDICATED

AS

A SLIGHT TOKEN OF GRATITUDE

FOR

THE INSTRUCTION AND MANY KINDNESSES

RECEIVED BY

THE AUTHOR.

PREFACE.

In presenting the result of my observations on Fichtelit I have found it often necessary to allude to several other fossil resins which are very similar to it.

I have given a short historical notice of these, and have also alluded to the points which they possess in common; showing that some of them, which are now considered distinct, are probably identical in composition.

I was unable to make any direct comparison of these resins with Fichtelit, for they are all very rare, and seldom found in large quantity. This fact prevents a careful revision of the subject of fossil resins by one person.

These investigations were made during the winter of 1856—57 in the laboratory of Professor Liebig. To him I am not only indebted for the assistance rendered me during their prosecution, but also for the instruction and kindness received during the two years that it has been my pleasure to be in his laboratory.

To his former most able assistant Dr. Mayer my most sincere thanks are due for the interest he has taken in my studies.

To Professor Kobell, by whom the crystal measurements were verified, I am much indebted for the aid rendered me. Finally I may be allowed to express my gratitude to Professor Wöhler for the assistance afforded me in the presenting of this dissertation.

May, 27th.

The rare fossil resin, which is the occasion of this paper and which I obtained for analysis through the kindness of Professor Liebig, was received from Mr. Fikentscher of Redwitz in the north of Bavaria.

In that region are beds of turf several feet in thickness, which contain large quantities of wood — stems and branches — in various stages of preservation.

The greater portion of this in pine wood, which is so little changed after lying in these turf beds for certainly hundreds of years, that to all appearance, except that it has become quite dark in color, it does not differ from well dried wood of the same species which is still growing in the vicinity. It cuts and splits the same, burns about as well, and is little inferior in troughness.

Professor Unger[1], who has made a microscopic examination of this wood, says that it evidently belongs to the still living species *Pinus sylvestris;* that it is very well preserved, but that in certain parts of the larger vessels a peculiar change has taken place, which has caused the walls of these vessels to lose their coherence and texture.

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[1] Annalen d. Physik u. Chemie. Vol. LIX, p. 55.

The other woods found in these turf beds are in a much worse state of preservation.

The remains of birches (Betula alba), alders (Alnus glutinosa), and hazelnut (Corylus avellana) are quite numerous.

The same species exist at present in the neighbourhood.

It is in this pine wood, which is still growing so plentifully as to give a name to the mountains of north Bavaria (Fichtelgebirge), that this fossil resin is found.

It occurs principally in the form of shining scales between the annual rings, which have separated from one another. The method of extracting it, and its crystaline form we will consider farther on.

In 1837 Trommsdorff[1] received from Mr. Fikentscher a fossil resin, which was found under exactly the same circumstances, in the well preserved stems of buried pines.

The analysis, which he caused to be made, shows however that it is the same substance which was found some years later in a brown coal bed near Utznach in Switzerland, and that it differs both in its composition and in its melting point, 107° C., from the resin which we have analyzed.

In 1841 Bromeis[2] examined a fossil resin, which was also received from Mr. Fikentscher, and which was found, like the previous, in the light brown colored pine stems, between the annual rings, often in the form of

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[1] Annalen d. Phar. Vol. XXI, p. 126.

[2] Annalen d. Phar. Vol. XXXVII, p. 304.

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flat prismatic crystals, colorless and without taste or smell.

It proved however to be quite distinct from that analyzed by Trommsdorff, both in its composition and in its melting point, 46° C. Bromeis proposed the name Fichtelit for this.

In 1843 Schrötter[1] became possessed of a fossil resin also from Redwitz. This was extracted from the wood by ether, and allowed to crystalise, when it was found to be composed of two substances, one of which could not be crystalised, but went down as an oil. This he considered to be identical in composition with Fichtelit; but erroneously, for he overlooked the fact that in the analysis by Bromeis the old atomic weight of carbon is used.

The crystaline portion of the resin received by Schrötter contained oxygen as well as carbon and hydrogen.

From this we see that at least three or four different carbo-hydrogen fossil resins have been obtained from the turf beds of Redwitz; and all have been found in the well preserved stems of this one species of pine tree.

But the same has been remarked in other places where similar fossil resins have been found.

In the neighbourhood of Utznach in Switzerland is a bed of brown coal from two to three feet in thickness, which contains numerous remains of pines, firs, birches and other trees, in various stages of preservation. The pine stems are almost unchanged.

[1] Annalen d. Phys. u. Chem. Vol. LIX, p. 55.

This bed of coal has long been considered to belong to the tertiary formation, and is so spoken of by those who have noticed the fossil resins found in it.

The remarkable state of preservation of the pine wood, and the occurrence of fossil resins in it, identical with or very similar to those discovered in the pine stems of the turf beds of Redwitz, lead me to investigate more closely as to the relative age of this bed of brown coal.

I found that an examination of the plants contained in it has recently been made by Professor Heer[1], who has published a fine work on the "Tertiary Flora of Switzerland".

He remarks that "the pine which Göppert describes as *Pinites sylvestris*, is evidently the same which we have in our brown coal at Utznach, and which is in every respect not to be distinguished from our living pines. The same is true of the birches and firs. We have found very few animal remains, but these appear to belong to species which still exist with us."

Thus showing, as I anticipated, that this brown coal is of the same age as the turf beds of Redwitz.

Stromeyer[2] was the first to call attention to the existence of a fossil resin found in the wood preserved in this coal bed. To this he gave the name Scheererit. It was discovered in the cracks and between the annual layers of the bituminous wood.

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[1] Neues Jahrbuch für Mineral. u. Geol. v. Leonhard u. Bronn, 1846, p. 213.

[2] Kastner's Archiv. Vol. IX, p. 113.

Later in 1828 Könlein[1], who had charge of the working of this bed of coal, described a resin which he had discovered as early as 1822 in the stems of pines occurring in the brown coal.

For this, not knowing that Stromeyer had already described a fossil resin from the same bed, under the name of Scheererit, he proposed the name of "Naphtaline resinense prismatique", from its resemblance to naphtaline.

Neither Stromeyer nor Könlein gave an analysis of the resin which they described.

In 1829 Macaire Princep[2] analyzed a resin which he, like Stromeyer, had received from Colonel Scheerer, as coming from the brown coal bed of Utznach. Its melting point was found to be but two degrees lower than that of Fichtelit. Macaire Princep accepted the name Scheererit which Stromeyer had proposed.

Farther in 1838 Kraus[3] analyzed a substance which he had obtained from the same locality and which had been found in the well preserved pine stems.

This resin in appearance resembled Scheererit, but the analysis showed it to be different in composition.

In this as well as in the melting point it does not differ materially from the substance analyzed by Trommsdorff, which was found in the turf beds of Redwitz.

Schrötter, who considers the two idential, proposes the name Könlit for them.

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[1] Ann. d. Phys. u. Chem. Vol. XII, p. 336.

[2] Ann. d. Phys. u. Chem. Vol. XV, p. 294.

[3] Ann. d. Phys. u. Chem. Vol. XLIII, p. 141.

While Scheererit distills undecomposed, Könlit yields a substance which melts by the warmth of the hand, and has a composition perhaps identical with that of Tekoretin, which we have yet to notice. Kraus proposed the name Pyro-Scheererit for this latter.

Later Haidinger[1] in an article comparing the crystaline form of Hartit with that of what he supposed to be Scheererit, and which he had received from Utznach, remarks that the latter melts at 46 ° C.

Steenstrup[2], who has written considerably on the marshes and coal beds of Denmark, discovered in the stems of the pine trees, which are found in these in an almost perfect state of preservation in the neighbourhood of Holtegard, a fossil resin which was supposed to be Scheererit. The other woods occurring with this pine (P. sylvestris) are the same as those of Redwitz and Utznach.

The resin found by Steenstrup was shown by the analysis of Forchhammer to be composed of two carbohydrogens, and both quite distinct from Scheererit. They were separated by dissolving in boiling alcohol and allowing to crystalise. Tekoretin, being less soluble than Phylloretin, crystalised first. The former melts at 45 ° C. — the latter at 87 ° C.

From this cursory view of the different carbo-hydrogens discovered in the three localities which have been mentioned, we perceive that in each place a fossil resin occurs which melts at 45° or 46° C. — viz. Fichtelit described by Bromeis from Redwitz, Scheererit (?) by Haidinger from Utznach, and Tekoretin by Forchhammer from Holtegard.

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[1] Ann. d. Phys. u. Ch. Vol. LIV, p. 261.

[2] Videnskab. Selskabs naturvid. og Math. Afhandlinger. 9 Deel. 1842.

The relation which they bear to one another, through their actual composition, will be noticed later.

We have still another locality to mention where a fossil resin is found, from the fact that this fossil, which was analyzed by Schrötter[1], was considered by him to be very similar to Scheererit and to have the same composition as Tekoretin.

In 1841 Haidinger[2] discovered a fossil resin resembling Scheererit in the brown coal beds of Oberhart not far from Vienna. One part of these beds contains numerous stems of a sort of pine tree, which are preserved either as bituminous, or as petrified wood i. e. quarz in the form of wood.

In the different layers and cross breakings of these stems the resin which is called Hartit is found.

These coal beds have at present an inclination of 70°, and are considered to belong to the tertiary formation.

The pine wood in which the resin occurs was examined by Unger[3] and pronounced to belong to the species *Peuce acerosa* Ug., which is very common in the brown coal formation. Hartit, which was analyzed by Schrötter, melts at 74° C.

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[1] Ann. d. Phys. u. Chem. Vol. LIX, p. 37.

[2] Ann. d. Phys. u. Chem. Vol. LIV, p. 261.

[3] Ann. d. Phys. u. Chem. Vol. LIX, p. 41.

This is the only carbo-hydrogen fossil found in the coal beds of Oberhart, while at Redwitz there are at least two; at Utznach three have been described, including one derived from the distillation of Könlit; and from Holtegard two have been analyzed by Forchhammer.

We have thus briefly alluded to the various fossil resins found in the four different localities mentioned, because it will be necessary to speak of the relation which they bear to one another and to the substance which we have analyzed.

As to the actual composition of several of these fossils much doubt exists, for most of the analyses were made at a time when the atomic weight of carbon was considered to be 6.125, and the method of analysis was much less perfect than at present.

We shall now proceed to notice more specially the substance which we have received for analysis; beginning first with it appearance in the wood, and the mode of extracting and crystalising it, together with its crystaline form; next the action of various reagents upon it; then its composition and relation to other similar resins which have been mentioned; and finally its chlorine and bromine compounds.

This substance occurs principally between the annual rings of the wood, which have separated or are still loosely joined to one another. Here it forms layers, often one tenth of an inch in thickness, of shining transparent scales, having more or less of a yellowish tinge, and lapping one over the other. These exhibit when held in the proper light, that peculiar ramified appearance shown by frost on window panes.

In some parts of the wood are what appear to be minute granules of this resin mixed with woody matter, but when examined under the microscope they prove to be small crystals, with their faces obliquely inclined to one another. I did not succeed in finding any large and regular enough for determining the crystaline form.

But this substance is not confined to the annual layers; for if the wood is split in any direction whatever, numerous shining points appear, showing that it is completely saturated with it.

In order to obtain this from the wood the latter is finely cut up with a turning lathe, or by any other convenient means, and then boiled in ether for several hours. The extract is then poured off, fresh ether is added, and again submitted to two or three hours boiling. The two extracts are now poured together and considerably concentrated by distilling off a part of the ether. Strong alcohol is added to this till all remains dissolved.

From this it was found impossible to obtain crystals, although exposed to a temperature below 0° C., a reddish oil went down instead.

So in order to separate the resin from other organic bodies, which were presumed to be present, and which were supposed to prevent the forming of crystals, the acetate of lead was added. The large and heavy precipitate, which went down, was thrown on to a filter, and the filtrate, after being freed from the excess of acetate of lead by sulphuretted hydrogen, and boiled with the precipitate for a time to decolorise it, was exposed to a cold of a few degrees below 0 °C., when long prism shaped crystals were formed.

Any foreign substance, or a crystal of this resin thrown into the alcoholic solution, assists the first forming of crystals very materially.

Before cutting up the wood it is best to scrape off as much resin as possible, for this portion dissolved in alcohol and ether, crystalises quite easily.

The precipitate occasioned by the acetate of lead, which is not soluble in ether, was mixed with alcohol and decomposed by a current of sulphuretted hydrogen. In the filtrate of this new precipitate crystals were formed when exposed to a temperature below 0 °C. These we have not yet examined.

CRYSTALINE FORM.

We now come to the crystaline form of this fossil resin.

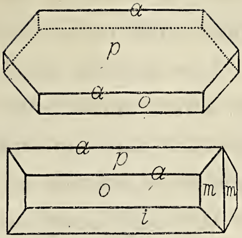
The crystals are oblique rhombic prisms with orthodiagonal faces. Sometimes an oblique end face is present behind. In the prevailing form the angles of the side faces $m : m = 97°$ and $83°$: the end face p to the orthodiagonal face $o = 127°$: the second oblique end face behind $i : o = 128°$; and $p : i = 105°$.

The orthodiagonal face cuts off the acute side angle of the prism *m*.

The crystals are lengthened in the direction of the orthodiagonal: *m* in mostly very short.

If the face *p* is adjusted in the stauroscope with the sides *a a* the cross stands normal; a proof that the crystalisation is not triclinic.

The measurements could only be made by the reflection of candle light with the use of the lens.



MELTING AND BOILING POINTS.

The melting point is 46 ° C., but the temperature at which this substance solidifies again is much lower viz. 36 ° C., making a difference of ten degrees between the melting and freezing points. These observations were carefully made by exprimenting on several different portions of the resin.

This somewhat strange behaviour has already been observed in other bodies e. g. Oleaic acid when melted does not solidify till cooled to 4 ° C.; its melting point is 14 ° C.: Doeglinic acid which melts at 16 ° C. congeals a few degrees above 0 ° C.

To determine the boiling point of this substance about five grams were put into a small retort holding a thermometer running up to 320 ° C. The latter was lowered almost to the surface of the melted resin, and the heat gradually increased till the mercury reached 310 °, when the thermometer was taken out, and the retort more strongly heated. Soon oil drops began to collect in the neck of the latter, which on cooling assumed more or less of a crystaline structure.

The distilled portion when dissolved in alcohol and and ether crystalised like the original substance and possessed the same melting and freezing points; showing that it suffered no change by distillation.

We may safely say that the boiling point is above 320 ° C., for the thermometer was rapidly rising when it was taken out.

A peculiar but agreeable odor was given out during the distillation, and a small part of the resin was decomposed, accompanied by the separation of coal.

ACTION OF SULPHURIC AND NITRIC ACIDS.

Anhydrous sulphuric acid produces a total decomposition of the substance. A small portion was put into a test tube, and to this the sulphuric acid was added, when, although cold, a violent reaction took place, fumes of sulphurous acid were given out, and the whole tube was blackened with coal.

To another portion Nordhausen acid was added, and then heated in the water bath. Sulphurous acid was slowly given out, and the solution became deep red.

In order to see if any combination with sulphuric acid had taken place, water was added and the whole heated with carbonate of baryta. The precipitate was separated, but the filtrate, which was greatly concentrated by evaporation, yielded no crystals of any soluble salt of baryta.

This experiment was often made in different ways, but without obtaining any combination with sulphuric acid.

To another portion of this resin fuming nitric acid was added, and heated carefully in the water bath. Soon a violent reaction took place, red fumes of nitrous acid were given out in large quantity. After the action of the nitric acid was finished, the whole was evaporated to one third its volume, and water added, causing a white precipitate. This was thrown on to a filter, washed out, and dissolved in alcohol and ether. The reddish solution was boiled with animal carbon to decolorise it, and then exposed to a temperature several degrees below 0 ° C. But instead of crystals being formed, an oily substance, which probably holds nitrous acid, was sent down as the ether evaporated.

The filtrate of the precipitate caused by the action of water on the nitric acid solution, was evaporated to dryness over the water bath, and the residue dissolved in a little water.

To one portion of this ammonia and chloride of calcium were added. giving a precipitate of oxalate of lime.

To another portion ammonia and chloride of barium were added, giving a precipitate of oxalate of baryta.

With another part ammonia and a solution of sulphate of lime gave also a precipitate of oxalate of lime. Showing that oxalic acid is one of the products formed by the action of nitric acid on this resin.

If this substance is thrown into cold fuming nitric acid and allowed to stand for two or three days it dissolves entirely; but when precipitated from this solution by water, and dissolved in alcohol and ether, it behaves like the last, going down as a reddish oil.

A mixture of fuming nitric and sulphuric acids seems to act like nitric acid alone.

Although we have not succeeded in obtaining combinations with nitrous acid, which we know to be such, yet we do not doubt but that they are formed, from the fact that they have been obtained from other substance which are very similar to this.

ACTION OF CHLORINE AND BROMINE.

Chlorine gas in contact with this resin in a melted state combines with it. The experiment is best made by putting a few grams in a small Liebig's drying apparatus, the lower part of which runs horizontally. This is placed in a water bath, the temperature of which must be kept above 46° C. With this bent tube a retort, in which chlorine gas is generated, is connected.

A higher or lower compound of chlorine is formed, in accordance with the length of time that the gas is passed over the melted substance; or two or three compounds may be formed at the same time. Fumes of hydrochloric acid appear at the open end of the tube.

The action of bromine is of course similar to that of chlorine. Hydrobromic acid is given out, and higher or lower compounds are formed, as the quantity of bromine used is greater or less. The substance should be melted in a flask and the bromine added from time to time.

ANALYSIS OF SUBSTANCE.

It was obtained pure for analysis by several re-crystalisations from its solution in alcohol and ether.

The combustions were made with chromate of lead, and with rolls of fine oxydized copper wire in the front part of the tube.

Three out of several analyses are here given.

I. 0,3324 grm. of substance gave
1,0591 ,, carbonic acid and
0,3819 ,, water.
II. 0,4314 ,, of substance gave
1,3761 ,, carbonic acid and
0,4980 ,, water.
III. 0,4008 ,, of substance gave
1,2859 ,, carbonic acid and
0,4689 ,, water.

These give the following percentages:

	I.	II.	III.
Carbon	86.89	87.00	87.50
Hydrogen	12.76	12.83	12.99

The average of the three and the corresponding formula are as follows,

	Average.	Calculated.	
Carbon	87.13	C_8	87.27
Hydrogen	12.86	H_7	12.73

This gives as the empirical formula for this resin $C_8 H_7$. — The other analyses confirm this result.

We will now proceed to compare this formula with those obtained by others for several of the fossil resins already mentioned, viz. with Fichtelit analyzed by Bromeis, with Hartit analyzed by Schrötter, and with Tekoretin and Phylloretin analyzed by Forchhammer.

But first we must allude to a matter which has given us no little trouble.

All the above mentioned resins with the exception of Hartit were analyzed when the atomic weight of carbon was held to be 6.125, hence too much carbon was almost always obtained in an analysis.

Now in books on organic chemistry, and in chemical journals when these fossils are alluded to, this fact seems generally to have been overlooked.

We will give two or three instances out of the very many which we have noticed.

Schrötter [1] who analyzed Hartit compares his results with those obtained by Forchhammer for Tekoretin, and remarks that the two substances are very probably identical in composition, and only differ in their melting points. We give the results as obtained by each:

	Hartit.	Tekoretin.
Carbon	87.47	87.19
Hydrogen	12.04	12.81.

Now if we overlook the fact that in the analysis of Hartit the atomic weight of carbon was taken as 6., but in the analysis of Tekoretin as 6.125, then Schrötters remark seems to be correct. The actual difference in composition will be seen if we in both cases take the atomic weight of carbon as 6.

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[1] Ann. d. Phys. u. Chem. Vol. LIX, p. 44

Hartit.	Tekoretin.
87.47	85.89
12.04	12.81.

Again Gerhardt[1] commits the same error, but in a different way. On noticing Scheererit (Könlit) he gives the composition in one hundred parts as obtained by Kraus, who took the atomic weight of carbon as 6.125, but affixes to this a formula in which it is taken as 6: e. g.

		nC^2	H
Carbon	92.45	92.	3
Hydrogen	7.42	7.	7

Tekoretin, Phylloretin and other resins are noticed in the same way by Gerhardt.

Löwig in his "Organic Chemistry" has many similar errors. The same oversight is also common in works on mineralogy.

COMPARISON WITH OTHER SIMILAR FOSSIL RESINS.

Let us now compare the result which we have obtained with the composition of several similar fossil resins. Those analyses which were made when the atomic weight of carbon was held to be 6.125 we have recalculated.

The four substances which bear perhaps the nearest relation to that which we have analyzed, are Fichtelit, Hartit, Tekoretin and Phylloretin. Their composition in one hundred parts is

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[1] Traité de Chemie Organique, Tome quatrième, p. 398.

Fichtelit.	Hartit.	Tekoretin.	Phylloretin.
87.95	87.47	85.89	88.88
10.70	12.04	12.81	9.22.

They require probably the following formulæ, Fichtelit C_5H_4, Hartit C_6H_5, Tekoretin CH, Phylloretin C_3H_2.

Though the numbers obtained by the analysis of Fichtelit by Bromeis indicate a different formula, yet we are disposed to consider it identical with the substance which we have analyzed; for they both occur under the same circumstances and in the same turf beds; and moreover they have a common melting point. Fichtelit also distills without being decomposed, and behaves towards alcohol and ether as does this resin.

The difference in composition, indicated by the analyses, may perhaps be accounted for by the fact that Bromeis analyzed Fichtelit just as it was obtained from the wood, without recrystalising it, hence it was necessarily impure.

Rather than increase the confusion already existing in the nomenclature of these and allied substances, we shall adopt the name given by Bromeis.

We should not forget to notice that Trommsdorff has also analyzed a fossil resin coming from Redwitz and found under the same circumstances, in the stems of *Pinus sylvestris,* and having the same outward appearance as Fichtelit, but in its melting point, 107° C., and in its composition it differs greatly; viz.

	Könlit (?)
Carbon	91.05
Hydrogen	7.57.

The formula obtained for Hartit stands nearer that of the fossil resin which we have analyzed; its crystals are also monoclinic; towards alcohol, ether, and sulphuric acid it behaves the same; and during distillation but a small portion is decomposed; but its melting point is much higher, 74° C., besides it occurs in another fossil pine, *Peuce acerosa* Ug., and in another geological formation, being as to its origin much older.

Tekoretin resembles this resin in every particular except in composition. Its melting point is 45° C; it distills at nearly 336°; possesses the same solubility in alcohol and ether; the effect of nitric acid and chlorine gas in the same, building two compounds with the latter, which Forchhammer did not succeed in separating; and it is also found in the buried stems of *P. sylvestris;* but the formula required by its analysis obliges us for the present to consider it as another resin.

Phylloretin, which like the latter is found in the pine stems in the marshes of Holtegard, though distilling at a high temperature and forming compounds with chlorine, differs not only in composition, but in its melting point, 87° C., from the fossil resin which we have described.

We have still another carbo-hydrogen resin to notice, which was the first described of all these in 1827. This was called Scheererit. It melts at 44° C. and distills, without being decomposed, at 90° C.

Some confusion exists with regard to this fossil, from the fact that Kraus[1] has given the analysis of a substance under the name of Scheererit, which had it is true been obtained from the coal beds of Utznach, like that described by Stromeyer and Macaire Princep, but which melts at 107°C.; is decomposed by distillation, and has a composition quite different from Scheererit as given by Marcaire Princep:

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[1] Ann. d. Phys. u. Chem. Vol. XLIII, p. 141.

	Scheererit.
Carbon	71.91
Hydrogen	24.00.

The inexactness of the analysis leaves much doubt as to its true composition. The substance was very volatile, and only one analysis was made. Macaire Princep himself was not satisfied with the result. Since he made the analysis no substance has been found in the coal beds of Utznach which melts at 44° C. and distills at 90° C.

We give here a table of those fossil resins to which we have referred, together with their melting and boiling points, and also the effect of chlorine, nitric and sulphuric acids on them. We have thought the percentage of carbon and hydrogen found would give a better idea of the relation of these fossils to one another, than their formulæ, for many of the latter, deduced from the amount of carbon and hydrogen obtained, are doubtful.

	Carbon.	Hydrogen.	Melting Point.	Boiling Point.	Effect of Chlorine.	Of Nitric Acid.	Of Sulphuric Acid.
Fichtelit by Bromeis	87.95	10.70	46°C.	Unknown, not decomposed.	Unknown	Unknown.	Unknown.
Fichtelit by Clark	87.13	12.86	46°C.	Above 320°C.	Combines	Oxalic acid, and NO_4 combination (?)	Blackened.
Tekoretin	85.89	12.81	45°C.	Of quicksilver.	do.	do.	Unknown.
Scheererit by Haidinger	Unknown	Unknown	46°C.	Unknown.	Unknown	Unknown.	do.
Scheererit by Princep	71.91	24.00	44°C.	90°C.	do.	do.	Blackened.
Hartit	87.47	12.04	74°C.	Very high.	do.	do.	do.
Phylloretin	88.88	9.22	87°C.	Of quicksilver.	Combines	Oxalic acid, and NO_4 combination (?)	Unknown.
Könlit(?) by Trommsdorff	91.05	7.57	107°C.	Unknown, not decomposed.	Unknown	No effect.	Blackened.
Könlit by Kraus.	91.12	7.42	114°C.	At 200°C, decomposed.	do.	Dissolves it.	do.

CHLORINE AND BROMINE COMBINATIONS.

The rational formula for any one of the fossils which we have mentioned has not yet been determined.

We only know the empirical formula. None of the products resulting from their combination with chlorine, bromine, sulphuric or nitrous acids have been analyzed.

For this purpose we have formed and analyzed several chlorine and bromine combinations of this resin.

Chlorine gas was passed over a few grams of it as already described, for the space of one half hour. It was then dissolved in alcohol and ether, and stood in the cold to crystalise. After standing several days, all the undecomposed resin crystalised out, and soon a clear transparent oil began to go down.

The mother liquor was now poured off, and another attempt was made to crystalise this oil from its solution in alcohol and ether; but though exposed for many nights to a temperature several degrees below 0° C., still no crystals were formed, but this oil appeared again.

The mother liquor was allowed gradually to evaporate till the clear colorless oil, which was sent down, began to be of a somewhat yellowish tinge. From this the mother liquor was poured off, and the oil redissolved in alcohol and ether, and again allowed to evaporate till two thirds of that which had been dissolved was precipitated. This was perfectly clear, transparent, and colorless. The mother liquor was again poured off, and the oil again treated with alcohol and ether.

It was then transferred to a watch glass, — put under the air pump, together with pieces of caustic potash, —

the air pumped out, and then allowed to stand for several days. The oil on being transferred to the watch glass was mixed with air and alcohol, and lost its transparency and clearness. These however returned upon its standing for some time. — The mother liquor of this oil was treated in the same way. A yellow transparent oil was obtained, but in too small a quantity for analysis.

Over another portion of fossil resin a stream of chlorine gas was passed for two hours. This was then dissolved in alcohol and ether as the last. Two oils were obtained, neither of which could be crystalised. The one which was first precipitated was of a deep yellow color and perfectly clear; the other was of a dark red color. There was too little of the latter for analysis.

ANALYSIS OF THE CHLORINE AND BROMINE COMBINATIONS.

For determining the amount of chlorine and bromine contained in the oils obtained, the combustions were made with caustic lime. For determining the amount of carbon and hydrogen simply chromate of lead was used, having the combustion tube longer than usual.

Before giving the results obtained, I must remark that it is greatly to be regretted that I did not succeed in obtaining these combinations in a crystaline form; for then there could be no doubt as to their purity. As it is, a small portion of this resin may have been held in solution by the oils, and so of course have affected the results obtained. I therefore present the following analyses with the hope that some one may hereafter be more fortunate than I have been in forming crystaline combinations of this resin with chlorine and bromine.

FIRST CHLORINE COMBINATION.

I. 0.4192 grm. of substance gave
1.1868 „ carbonic acid and
0.4216 „ water.
II. 0.6903 „ of substance gave
0.3156 „ chloride of silver.

Hence

	Calculated.		Found.
C_{80} =	480.00 —	77.555 —	77.213
H_{68} =	68.00 —	10.987 —	11.173
Cl_2 =	70.92 —	11.458 —	11.304
	618.92		

SECOND CHLORINE COMBINATION.

I. 0.3933 grm. of substance gave
1.0013 „ carbonic acid and
0.3443 „ water.
II. 0.5411 „ of substance gave
0.4432 „ chloride of silver.

Hence

	Calculated.		Found.
C_{80} =	480.00 —	69.783 —	69.433
H_{66} =	66.00 —	9.595 —	9.726
Cl_4 =	141.84 —	20.621 —	20.250
	687.84		

In order to obtain bromine combinations the resin was acted upon by bromine as previously described, and dissolved in alcohol and ether. After standing several days in the cold most of the time below 0° C. the undecomposed substance had entirely crystalised out, and a light red oil began to go down. By treating the mother liquor as in the case of the chlorine compounds two oils were obtained; one of a light red color and perfectly clear, the other dark red and much more consistent.

It is quite difficult to get these oils pure and unmixed. The color of the oil, which is first precipitated, must be closely observed, and when this changes, a mixture has taken place.

FIRST BROMINE COMBINATION.

I. 0.4169 grm. of substance gave
1.1646 „ carbonic acid and
0.4151 „ water.
II. 0.3909 „ of substance gave
1.0886 „ carbonic acid and
0.3867 „ water.

Hence

	Calculated.		Found. I.	Found. II.
C_{80} =	480.00	76.315	76.186	75.95
H_{69} =	69.00	10.970	11.063	10.99
Br =	79.97	12.715	12.751	13.05
	628.97.			

SECOND BROMINE COMBINATION.

0.4823 grm. of substance gave
0.257 „ bromide of silver.

Hence

	Calculated.		Found.
C_{80} =	480.00	67.801	
H_{68} =	68.00	9.605	
Br_2 =	159.94	22.592	22.673
	707.94.		

We have thus obtained the four following formulæ for the chlorine and bromine compounds:

$C_{80}H_{69}Br_1$, $C_{80}H_{68}Br_2$, $C_{80}H_{68}Cl_2$, $C_{80}H_{66}Cl_4$.

Hence the rational formula for this fossil resin would seem to be

	Calculated.		Found.
C_{80} =	480.	— 87.273	— 87.13
H_{70} =	70.	— 12.727	— 12.86
	550.		

This is of course quite an unexpected result, although the rational formula for none of these fossil resins has previously been determined. Other carbohydrogen substances have however been described with very high formulæ, e. g. *Melene* and *Cerene*. The formula for the former is C_{60} H_{60} — and for the latter C_{54} H_{54}. Moreover both of the substances, like that which we have analyzed, have many of the properties of Paraffine, and form compounds with chlorine.

There are two objections to reducing this formula to C_{40} H_{35}. The first is that it gives an uneven number of hydrogen atoms, and secondly that in the first bromine compound it requires one half an atom $(Br_{1/2})$ of bromine. Laurent and others have however expressed half atoms in various formulæ.

THE END.